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Fischer-Tropsch Catalyst for Aviation Fuel Production

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Abstract

As the oil supply declines, there is a greater need for cleaner alternative fuels. There will undoubtedly be a shift from crude oil to non-petroleum sources as a feedstock for aviation (and other transportation) fuels. The Fischer-Tropsch process uses a gas mixture of carbon monoxide and hydrogen which is converted into various liquid hydrocarbons; this versatile gas-to-liquid technology produces a complex product stream of paraffins, olefins, and oxygenated compounds such as alcohols and aldehydes. The Fischer-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur and aromatic compounds. It is most commonly catalyzed by cobalt supported on alumina, silica, or titania or unsupported alloyed iron powders. Cobalt is typically used more often than iron, in that cobalt is a longer-active catalyst, has lower water-gas shift activity, and lower yield of modified products. Promoters are valuable in improving Fischer-Tropsch catalyst as they can increase cobalt oxide dispersion, enhance the reduction of cobalt oxide to the active metal phase, stabilize a high metal surface area, and improve mechanical properties. Our goal is to build up the specificity of the Fischer-Tropsch catalyst while adding less-costly transition metals as promoters; the more common promoters used in Fischer-Tropsch synthesis are rhenium, platinum, and ruthenium. In this report we will describe our preliminary efforts to design and produce catalyst materials to achieve our goal of preferentially producing C_8 to C_{18} paraffin compounds in the NASA Glenn Research Center Gas-To-Liquid processing plant. Efforts at NASA Glenn Research Center for producing green fuels using non-petroleum feedstocks support both the Sub-sonic Fixed Wing program of Fundamental Aeronautics and the In Situ Resource Utilization program of the Exploration Technology Development and Demonstration program.

Nomenclature

Al_2O_3	alumina or aluminum oxide
<i>BET</i>	Brunauer, Emmett, and Teller, surface area analysis method
CH_4	methane or natural gas
CO	carbon monoxide
<i>Co</i>	cobalt
<i>CSTR</i>	continuously-stirred tank reactor
<i>EDS</i>	energy dispersive spectroscopy
<i>Fe</i>	iron
<i>FTS</i>	Fischer-Tropsch synthesis
<i>GTL</i>	gas-to-liquid
H_2	hydrogen gas
<i>ISRU</i>	In Situ Resource Utilization (program)
<i>Pt</i>	platinum
<i>RWGS</i>	reverse water-gas shift reaction
<i>Re</i>	rhenium
<i>Ru</i>	ruthenium
<i>SEM</i>	scanning electron microscopy
SiO_2	silica or silicon dioxide
TiO_2	titania or titanium dioxide
<i>TPR</i>	temperature-programmed reduction, a chemi-sorption analysis method
<i>WGS</i>	water-gas shift reaction

Introduction

Petroleum has made it possible to advance technology and modern transportation over the past two centuries. However, several realities have emerged to force a re-thinking of an over-reliance on this non-renewable fossil fuel: the environmental impact of their usage, complex geo-politics and security ramifications, and eventually the dwindling supply of this essential but non-renewable resource. While there are certainly alternatives to petroleum-based transportation such as fuel cell or other electric land and nuclear maritime propulsion, aviation and space transportation require high-energy-density fuels. Gas-to-liquid (GTL) technologies, notably Fischer-Tropsch (FT) processing of synthesis gas (CO and H_2), are critical industrial processes that produce a complex product stream useful for transportation fuels and chemicals. We describe efforts at NASA Glenn to produce Fischer-Tropsch synthesis catalysts that target the saturated hydrocarbon fraction of the product stream (C_8 to C_{18} hydrocarbons), as this material is most similar to the high-energy-density JP-8, an aviation fuel useful for commercial and military jets.

As the oil supply dwindles, there is a greater need for (cleaner) alternative fuels and/or feedstocks (Refs. 1 to 3). Also, there is likely to be a shift from crude oil to natural gas as a feedstock for the chemical industry. In order to meet the new demand, the FT processes will be critical for gas-to-liquid conversions. Fisher-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur and aromatic compounds (Refs. 4 to 5); it uses a feedstock of carbon monoxide and hydrogen (syn-gas), in which the gas is converted into various liquid hydrocarbons. Typically, FTS is catalyzed by cobalt supported on alumina, silica, or titania or unsupported alloyed iron powders. Cobalt is typically used more often than iron because cobalt is a longer-active catalyst, has less

water-gas shift activity, and lower production of modified products such as oxygen-containing molecules (alcohols, aldehydes, ketones, etc.) (Ref. 6).

One objective of the effort at NASA GRC is to develop multiple FTS catalysts to use in the Alternative Fuels Research Laboratory, a petroleum processing facility with three continuously-stirred tank reactors (CSTRs). The catalysts were prepared and fully characterized by various analytical techniques: chemical analysis, scanning electron microscopy, chemi- (temperature programmed reduction or TPR) and physi-sorption (Brunauer, Emmett, and Teller or BET) analysis. The goal is to enhance the fraction of the FTS reaction that can be used for aviation fuel (saturated C₈ to C₁₈ hydrocarbons) or additives. As we develop a better understanding of the correlation between the preparation and activity of catalysts, promoters are added to the supported FTS catalysts.

Addition of transition metals as promoters is one well-studied method to enhance the catalytic properties of FTS catalysts. The more common promoters used in FTS are rhenium, platinum, and ruthenium. Eri and co-workers were the first to add rhenium to cobalt/alumina catalysts (Ref. 7). Diaz and co-workers have shown that rhenium can enhance the reducibility of cobalt oxides as well as increasing catalytic activity (Ref. 8). Promoters are valuable in improving Fischer-Tropsch catalysts as they can increase cobalt oxide dispersion, promote reduction of cobalt oxide to the active metal phase, stabilize a high metal surface area, and improve mechanical properties (Ref. 9). In order to look for lower cost alternatives to the platinum-group metals we are looking at alternatives such as silver and manganese; platinum is also being studied as a comparison to the literature.

Efforts at the NASA Glenn Research Center for producing green fuels using non-petroleum feedstocks support both the Sub-sonic Fixed Wing program of Fundamental Aeronautics and the In Situ Resource Utilization (ISRU) program of the Exploration Technology Development and Demonstration (ETDD) program. The non-petroleum feedstocks include: bio-mass, salt-tolerant plants and algae, syn-gas, waste plastic, and gas streams derived from one or more second-generation waste conversion processes. The primary activities discussed herein include the synthesis and characterization of FTS catalyst with the addition of promoters as a means of improving the activity of the reaction.

Experimental

Catalyst Preparation

Catalysts were prepared in a similar manner to the description in a U.S. patent by Espinoza et al. (Ref. 10). Sasol Catalox SBA-200 alumina was used as a support material with a surface area of 192.12 m²/g and a pore volume of 0.46 ml/g. Cobalt (II) nitrate hexahydrate (Sigma-Aldrich) was used to load onto the alumina for the preparation of the cobalt FT Catalyst. Various promoters were added to this catalyst, which precursors included: tetraamine platinum (II) nitrate, silver nitrate, ruthenium (III) nitrosyl nitrate, palladium (II) chloride, manganese (II) nitrate hydrate, and nickel (II) nitrate hexahydrate. The support was calcined at 150 °C under 10⁻² torr in a vacuum oven. It was then maintained under atmospheric pressure of Argon at 150 °C until it was ready to be used. The alumina support was loaded with either 15 or 25% cobalt using the slurry impregnation method. This method involved doing two impregnations of the alumina with the cobalt solution leading to the desired loading. The loading solution used was 2.5 times the pore volume of the alumina support. The slurry was dried under vacuum with a rotary evaporator at 85 °C in between impregnations. After the final cobalt concentration was achieved, the noble metal promoter was added by incipient wetness impregnation, where the solution total volume was a mere 0.8 times the pore volume of the alumina. This was done to minimize the amount of noble metal loss and to account for the smaller pores, given that cobalt has partially filled these pores. The catalyst was then dried again under vacuum with the rotary evaporator. The catalysts were then calcined in dry air at 350 °C for 4 hr. Once the catalyst synthesis was complete, the catalyst are stable and stored under air in jars labeled appropriately.

TABLE 1.—FISCHER-TROPSCH CATALYSTS
[Cobalt on alumina support prepared by slurry
and incipient wetness impregnation.]

Sample number	Co loading, percent	Promoter, percent	ICP elemental analysis	Surface area, m ² /g	Reduction temperature, °C
1	25	No promoter		127.135	350
3	25	Ag 0.5	23.6/0.278	109.35	369
4	25	Mn 0.5	25.7/0.592	103.17	366
5	25	Ni 0.5	23.8/0.891	128.66	348
6	25	Ru 0.5	25.5/1.26	78.57	322
7	25	Pt 0.5	24.8/0.459	115.93	265
8	25	Ru 1.0	23.0/2.20	123.85	264
9	15	Mn 0.5	13.8/0.572	101.01	354
10	15	Pd 0.5	14.1/0.429	111.37	229

Surface Area Measurements

The BET (Brunauer, Emmett, and Teller) surface area was measured with a Micromeritics Flowsorb II 2300 and a Leeds and Northrup Automatic Surface Area Analyzer 4200. To eliminate water from the surface prior to measurement, the samples were degassed at 250 °C for about 30 min. The sample was then exposed to a 30% nitrogen mixture in argon while under liquid nitrogen. After a complete adsorption of nitrogen onto the surface of the catalyst was achieved, the sample was warmed up to room temperature and the amount of nitrogen desorbed was measured using a thermal conductivity detector (TCD). The results of the physisorption measurements are listed in Table 1.

Temperature Programmed Reduction

Temperature programmed reduction (TPR) was performed using a Micromeritics AutoChem II 2920 Chemisorption Analyzer. The TPR experiments were done in a 4% H₂/Ar gas mixture at a flow rate of 50 cm³. The sample was heated from 25 to 1000 °C at a ramp rate of 10 °C/min. The change in hydrogen was monitored by a thermal conductivity detector. The data is plotted as the TCD signal versus a change in temperature.

Scanning Electron Microscopy With Energy Dispersive Spectroscopy

Catalysts were analyzed using a Hitachi S-3000N scanning electron microscope (SEM) for imaging and energy dispersive spectroscopy (EDS) on EDAX Falcon to determine surface properties and elemental composition. The samples were loaded onto copper tape on the sample holder and then placed in the specimen stage where it would be evacuated to a high vacuum range of about 10⁻⁶ torr. The electron images were taken with an electron beam of 25.0 keV and viewed at various levels of magnification with a working distance of 14–25 mm. The elemental composition data was obtained by using SEM Quant ZAF microanalysis software in conjunction with the AMETEK- EDAX (EDAX, Inc., Mahwah, New Jersey) detecting unit, which uses a silicon drift detector for EDS.

Inductively Coupled Plasma—Optical Emission Spectroscopy

Samples were sent out to Galbraith Laboratories for confirmation of elemental analysis by inductively coupled plasma—optical emission spectroscopy. This technique is used for the quantitative detection of trace metals in a sample. The catalyst is digested in a mixture of nitric acid, hydrofluoric acid and hydrochloric acid, and then heated to 100 °C overnight (Ref. 11). The solution is then introduced to the plasma with a nebulizer in flowing argon carrier gas. This technique detects the emission of photons from each element as the atoms are relaxed to ground state energies. The ICP-OES was used to validate the metal loadings on the support for the cobalt and the noble metal promoters. This data is included in Table 1.

Results and Discussion

The preparations of the different catalysts were initially based on a description in a U.S. patent by Espinoza et al. (Ref. 10). and later modified by Jacobs et al. (Ref. 12). The initial phase catalysts were synthesized by combining the cobalt and the alumina in a beaker and allowing it to stir for 2 hr. The solution was then dried on a rotary evaporator, washed in water, re-dried in the rotary evaporator, further dried overnight at 150 °C, and finally calcined at 230 °C in dry air for 2 hr (Ref. 13). If a promoter was to be added, it would be added after calcination and then the sample would be re-calcined. Initial characterization of these catalysts revealed that the target weight percentage of the catalyst were not constant. Most samples lost over 50% of the cobalt in the washing procedure. While high dispersion was achieved, loss of material made this procedure undesirable to making successful catalyst. In improving the consistency and reproducibility of the catalyst synthesis, a more established method of slurry and incipient wetness impregnation was employed. Slurry impregnation was used when adding the cobalt to the bare alumina support. By dividing the cobalt into two batches and drying the catalyst between impregnations, we were able to maximize the amount of cobalt that was deposited into the pores of the alumina, thus improving our yield and dispersion. This method proved to be reliable as shown by the elemental analysis data in Table 1.

To this point, over 25 samples of heterogeneous Co on alumina catalyst materials have been prepared with different loadings of Co, various levels of dispersion, and different promoters at different loadings. Physi- and chemi-sorption data are included in Table 1. While we are just beginning to run these catalysts in the recently-commissioned Fischer-Tropsch CSTR facility, other characteristic techniques allow us to make preliminary conclusions as to the capability of the catalyst.

BET surface analysis has allowed us to correlate the surface area of the catalyst as cobalt and promoters are added. This data is displayed in Figure 1. It is established that the cobalt metal fills the pores of the alumina support (Ref. 14). This would lead to a reduction of the surface area of the originally 200 m²/g alumina support. This indeed was proven as the surface area was reduced to 127 m²/g by adding cobalt alone. When adding promoters to the catalyst, one would expect the pores to be mostly filled with the cobalt, thereby leaving the noble metals to sit on the surface. This was only proven to be true of the 0.5% Nickel sample. All other samples exhibited a reduction in surface area. This implies that the cobalt did not entirely fill the pores and the promoter metals did fall into the available space. It is expected that the higher the surface area of the catalyst, the better the catalytic activity in the FT reactor to produce fuel. However, this has not been established to date. Further studies on this are currently being pursued.

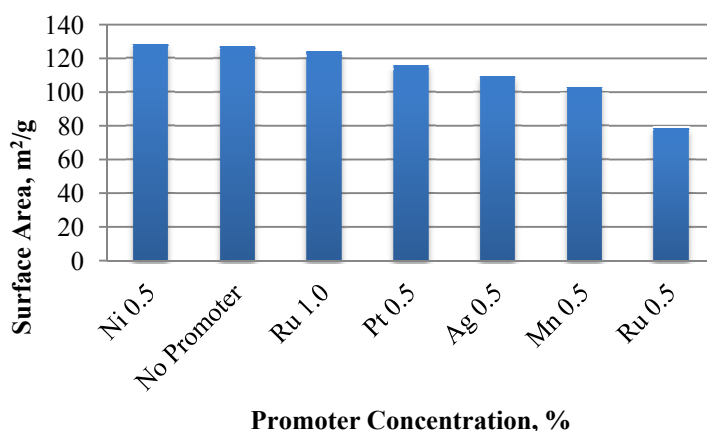


Figure 1.—Surface area of catalyst with varying promoter concentration. The change in surface area in m²/g is displayed with the various cobalt on alumina with promoters and their concentrations as well as a sample of cobalt on alumina without a promoter for reference.

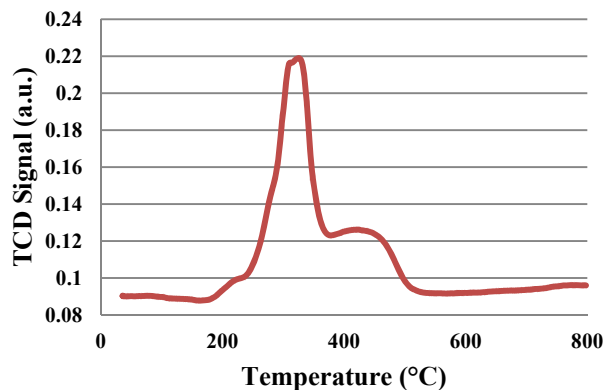


Figure 2.—TPR of cobalt on alumina promoted with 0.5% Pt. 4% hydrogen in argon was used and a temperature ramp up to 800 °C at 10 °C/min.

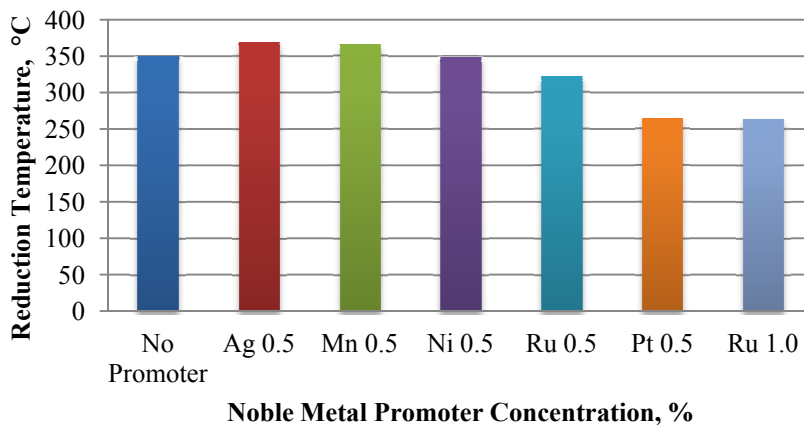


Figure 3.—Reducibility of catalyst with promoters. 25% Co on alumina with various noble metal promoters and their concentrations are represented.

Studies on these catalysts using temperature programmed reduction allowed us to monitor the activity of the catalyst in a blended gas of 4% H₂ in argon. Various peaks are typically seen on a cobalt on alumina sample. A lower temperature peak (around 200 °C) is indicative of nitrate coming off the surface. This gives direct evidence of the success of the calcination procedure. In Figure 2, a small shoulder is seen at about 210 °C. In our experiments, it has been shown that completely removing all traces of nitrate from the catalyst is not worth the effort. The peak at 310 °C represents the reduction of CoO to cobalt metal. This is the reaction that activates the catalyst to be used in the Fischer-Tropsch reactors. Our data, as seen in Figure 3, shows that Ru and Pt are better promoters than Ag, Ni, and Mn, as determined by lower reduction temperature in TPR.

By lowering the temperature at which the catalyst is reduced, the conditions of the activation for Fischer-Tropsch synthesis are more straightforward. The goal of adding promoters is to be able to reduce the activation temperature by adding the least amount of noble metal. The cost of these metals plays an important role in choosing the metal and the quantity used. It has been established that platinum is of the greatest benefit to FT catalysts (Ref. 14). However, its extremely high costs make it an undesirable promoter. Ruthenium is less expensive and has proven to provide a similar decrease in reduction temperature. Promoters can also aid in the dispersion of metal upon the alumina support. In order to document this, transmission electron microscopy needs to be explored; we currently are investigating this issue.

Additionally a concurrent study was performed to minimize the amount of cobalt needed on the surface. This study is in the preliminary stages and more samples are currently being synthesized. Surface area measurements, as shown in Table 2, demonstrate that addition of a promoter reduces the surface area. This indicates that the noble metals are becoming imbedded in the alumina pores. There was no real difference between the 25% cobalt and the 15% cobalt, with or without promoter. Through this one can conclude that the additional cobalt does not add value to the catalyst and thus the FT reaction. Further studies in the Alternative Fuels Laboratory are being done for more conclusive results.

The topographical SEM images provide a convenient method to monitor the morphology of the catalyst surface. The surface appears smooth with evenly dispersed particles. The shape and size of the catalysts particles are typically spherical and less than 50 μm in diameter. The data reveals that there is a correlation between the abundance of Co retained on the Al_2O_3 support and the method in which the Co is loaded onto the support. The method of two separate cobalt impregnations and avoiding excessive washing of catalyst seemed to produce a fine powder catalyst, which is recommended in order to obtain better cobalt dispersion on the surface of the alumina support. Figures 4 to 6 represent various cobalt catalysts with different levels of magnification. The detail here shows the evenly dispersed particles.

TABLE 2.—FT CATALYST WITH VARYING CO LOADING
[Co on alumina support.]

Sample number	Co loading, percent	Promoter, percent	ICP elemental analysis	Surface area, m^2/g	Reduction temperature, $^{\circ}\text{C}$
1	25	No promoter		127.135	350
2	15	No promoter	14.3	122.98	351
4	25	Mn 0.5	25.7/0.592	103.17	366
9	15	Mn 0.5	13.8/0.572	101.01	354
10	15	Pd 0.5	14.1/0.429	111.37	229

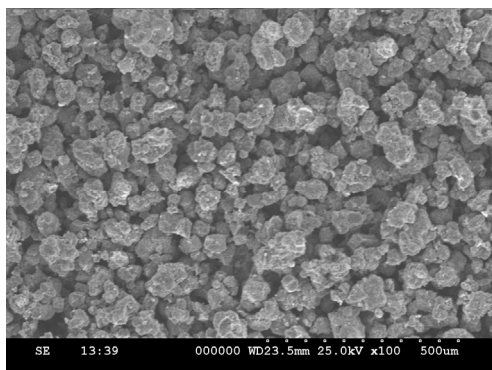


Figure 4.—SEM image of 1.0% Ru and 25% Co on Alumina. 100 \times magnification, catalyst made by slurry impregnation.

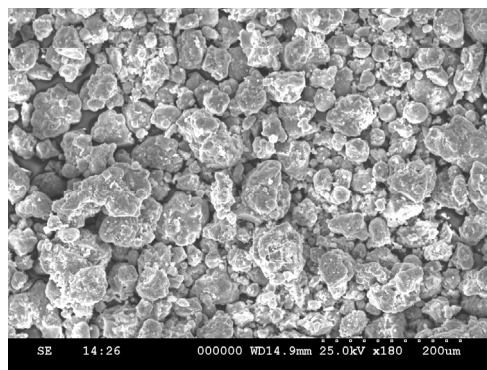


Figure 5.—SEM image of 0.5% Mn and 25% Co on Alumina. 180 \times magnification, catalyst made by slurry impregnation.

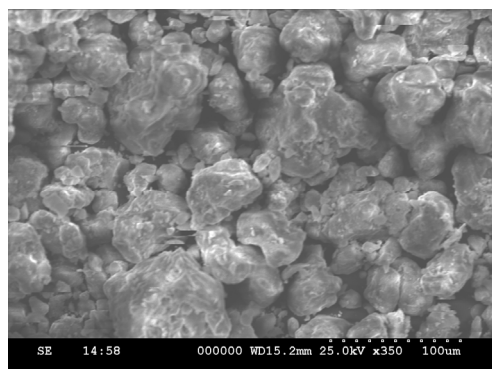


Figure 6.—SEM image of 0.5% Ru and 25% Co on Alumina. 350 \times magnification, catalyst made by slurry impregnation.

The catalysts were also analyzed for elemental weight composition via EDS. The percent of aluminum is directly related to the amount of $\gamma\text{-Al}_2\text{O}_3$ present in the catalysts. However, the percent of oxygen could be attributed to the presence of $\gamma\text{-Al}_2\text{O}_3$, CoO , or Co_3O_4 (Ref. 15). It is important to note that the percent of cobalt is representative of the amount of cobalt that has been deposited on the alumina support, which indicates that we have successfully synthesized $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ FT catalysts. The analysis for the promoter shows a range between 1.0 to 2.9%. EDS detected other components in the catalyst sample that were not in the experimental design and are probably impurities or chemical similarities of the components in the characterization. Representative spectra are shown in Figures 7 and 8.

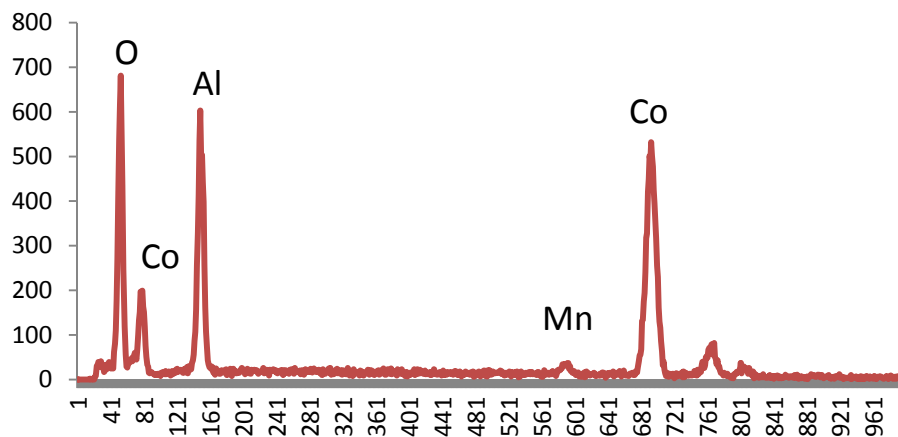


Figure 7.—EDS Spectrum of 0.5% Mn and 25% Co on Alumina.

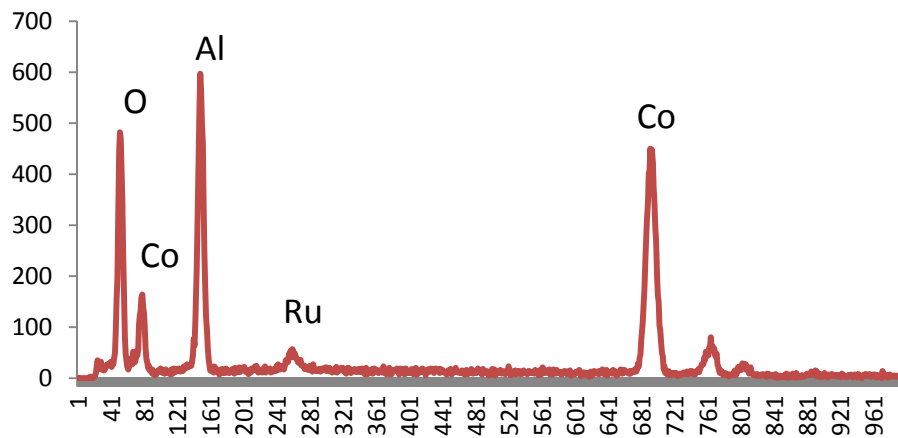


Figure 8.—EDS Spectrum of 0.5% Ru and 25% Co on Alumina.

Conclusions

Our characterizations verify that the synthesis of Co/ γ -Al₂O₃ catalysts for FT process is achievable at relatively low temperatures and mild reaction conditions. Since heterogeneous catalysis is a surface phenomenon, it is apparent that the extent of surface area of a solid will affect its catalytic activity because of the variation in the number of catalytic sites (Ref. 12). However, it is not obvious how the specific activity of a catalyst, such as the activity per surface site or per unit surface area, will depend on its state of dispersion.

EDS identified the composition of the catalyst but did not determine the precise target value due to the presence of impurities which affected the total percent of the sample components and to the necessity of correction factors. ICP resulted in more accurate values that were closer to the target values. The nickel promoted catalyst has the highest specific surface area followed by 1% Ruthenium. Additional experiments are necessary to elucidate precisely how each promoter is deposited on the surface.

Future work also involves the activation of the catalysts in the FT reactors located in the Alternative Fuels Research Laboratory to determine which promoter enhances the conversion of synthesis gas (CO and H₂) to hydrocarbons. The data collected here will be used to elucidate the effects of dispersion on the catalytic activity of Co/ γ -Al₂O₃ catalysts used for Fischer-Tropsch conversion (synthesis).

Clearly there are different issues surrounding non-petroleum feedstocks for aviation and terrestrial transportation fuels and ISRU processing of fuels to contribute to space exploration. However, whether the feedstocks for green aerospace fuels are syn-gas, common concerns to be addressed include: elimination and handling of (hazardous) by-products, energy efficiency and utilization, processing equipment reliability, overall cost effectiveness, and suitability for integration into a particular mission or application.

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14. ABSTRACT As the oil supply declines, there is a greater need for cleaner alternative fuels. There will undoubtedly be a shift from crude oil to non-petroleum sources as a feedstock for aviation (and other transportation) fuels. The Fischer-Tropsch process uses a gas mixture of carbon monoxide and hydrogen which is converted into various liquid hydrocarbons; this versatile gas-to-liquid technology produces a complex product stream of paraffins, olefins, and oxygenated compounds such as alcohols and aldehydes. The Fischer-Tropsch process can produce a cleaner diesel oil fraction with a high cetane number (typically above 70) without any sulfur and aromatic compounds. It is most commonly catalyzed by cobalt supported on alumina, silica, or titania or unsupported alloyed iron powders. Cobalt is typically used more often than iron, in that cobalt is a longer-active catalyst, has lower water-gas shift activity, and lower yield of modified products. Promoters are valuable in improving Fischer-Tropsch catalyst as they can increase cobalt oxide dispersion, enhance the reduction of cobalt oxide to the active metal phase, stabilize a high metal surface area, and improve mechanical properties. Our goal is to build up the specificity of the Fischer-Tropsch catalyst while adding less-costly transition metals as promoters; the more common promoters used in Fischer-Tropsch synthesis are rhenium, platinum, and ruthenium. In this report we will describe our preliminary efforts to design and produce catalyst materials to achieve our goal of preferentially producing C8 to C18 paraffin compounds in the NASA Glenn Research Center Gas-To-Liquid processing plant. Efforts at NASA Glenn Research Center for producing green fuels using non-petroleum feedstocks support both the Sub-sonic Fixed Wing program of Fundamental Aeronautics and the In Situ Resource Utilization program of the Exploration Technology Development and Demonstration program.					
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